ISSN 1070-4272, Russian Journal of Applied Chemistry, 2017, Vol. 90, No. 1, pp. 53−62. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © V.N. Sapunov, M.S. Voronov, S.I. Gustyakova, I.S. Kozeeva, E.M. Makarova, 2017, published in Zhurnal Prikladnoi Khimii, 2017, Vol. 90, No. 1, pp. 58−67.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Specific Process Features of Epoxidation of Fatty Acid Methyl Esters of Vegetable Oils with Performic Acid Generated In Situ

V. N. Sapunov*, M. S. Voronov, S. I. Gustyakova, I. S. Kozeeva, and E. M. Makarova

Mendeleev University of Chemical Technology of Russia, Miusskaya pl. 9, Moscow, 125047 Russia
**e-mail: sapunovvals@gmail.com*

Received December 27, 2016

Abstract—Physicochemical relationships of the phase distribution of the reactants in epoxidation of fatty acid methyl esters of vegetable oils with performic acid generated in situ were determined.. The progress of epoxidation is accompanied by redistribution of the organic and aqueous phase volumes. The major cause of changes in the phase volumes is the transfer of peroxide oxygen from the aqueous phase into the organic phase upon formation of epoxy groups. A comparable change in the phase volumes is due to reactive extraction of aqueous phase components with the epoxy compounds formed.

DOI: 10.1134/S1070427217010098

The modern trend toward production of environmentally friendly and biodegradable chemical goods leads to partial or complete replacement of traditional resources by renewable raw materials. Among such products, fatty acid methyl esters of vegetable oils (FAMEs) [1] and their epoxidized derivatives are of particular interest. These derivatives have already found use as plasticizers and stabilizers of polymer compounds, e.g., of those based on polyvinyl chloride (PVC) [2]. Peracids in the presence of an acid catalyst are often used as epoxidizing agents [3–6]. The reaction also occurs without catalyst [7].

The traditional process of epoxidation of vegetable oils and their FAMEs is based on using performic acid (PFA) prepared in situ in a two-phase system in which the aqueous phase contains hydrogen peroxide (HP) and formic acid (FA) and the organic phase contains unsaturated compounds [8, 9]. The main distinctive feature of such technology is the fact that the formation of epoxides is accompanied by an increase in the solubility in the organic phase of all the reactants initially present in the aqueous phase. This leads to changes in the phase ratio, which can affect the kinetics of the peracid formation and, correspondingly, the process as a whole. The decrease in the hydrophobicity of the organic phase in the course of the reaction corresponds to the concept of so-called “reactive extraction” [10, 11]. This effect is caused by the formation of stable clusters linked by strong hydrogen bonds [12]. The complex formed becomes a new active site in the organic phase, capable of aggregating other polar compounds, e.g., hydrogen peroxide, water, or formic acid, thus altering their concentrations in both phases [12].

The change in the solvating power of the organic phase in the course of the reaction negatively affects the epoxidation process parameters. For example, increased concentrations of water and acid in the organic phase make the process less selective because of epoxy ring opening [13]. In the industrial process, because of large heat release in the reaction (thermal effect –196 kJ per mole of hydrogen peroxide [14]), this effect is manifested in autoacceleration of the heat release, making it difficult to ensure stable operation of the reactors. Therefore, the use of this effect for optimizing the process in batch or continuous reactors or in a cascade of mixing reactors has become a subject of studies [15, 16].

This study was aimed at revealing the role of reactive extraction of the aqueous phase components with the epoxy compounds formed and at finding relationships in variation of the phase ratio in a two-phase process of epoxidation of FAMEs of vegetable oil with performic acid formed in situ.

EXPERIMENTAL

Experiments were performed with fatty acid methyl esters of rapeseed, sunflower, and flaxseed oils, freshly distilled at reduced pressure (170–175°C at 30 Pa). The esters were chosen so as to evaluate how the content of double bonds influences the epoxidation process. Each of the chosen esters contained a maximal amount of one of unsaturated acids: oleic ($C_{18/1}$), linoleic ($C_{18/2}$), or linolenic ($C_{18/3}$). The compositions of the fatty acid residues of FAMEs (wt %) were as follows: for rapeseed oil FAMEs, C_{16} 5.8, $C_{18/1}$ 56.5, $C_{18/2}$ 29.7, and $C_{18/3}$ 6.1; for sunflower oil FAMEs, C_{16} 6.5, $C_{18/1}$ 25.9, $C_{18/2}$ 56, and $C_{18/3}$ 1.4; for flaxseed oil FAMEs, C_{16} 6, $C_{18/1}$ 28.3, $C_{18/2}$ 17.8, and $C_{18/3}$ 47.8.

Formic acid [85 wt %, pure grade, GOST (State Standard) 5848–73] and hydrogen peroxide (37 wt %, medical grade, GOST 177–88) were supplied by Khimmed.

Iodometric titration was performed using a 0.1 N aqueous sodium thiosulfate solution (fixanal), potassium iodide (chemically pure grade, GOST 4232–77), and acetic acid, all supplied by Khimmed. Potentiometric analysis was performed by titration with an aqueous potassium hydroxide solution (0.18 N) using an ATP-02 automatic potentiometric titrator (Akvilon, Russia). Potassium hydroxide (analytically pure grade, GOST 24363–80) was supplied by Khimmed. The degree of epoxidation and the double bond content were determined with a Kristallyuks-4000 gas chromatograph (Khromatek, Russia). The samples of epoxidized FAMEs of vegetable oil were dried with a Heidolph rotary evaporator.

Epoxidation was performed in a 250-mL cylindrical glass reactor with a jacket, equipped with a reflux condenser, a thermometer, and a dropping funnel, with magnetic stirring. The temperature in the course of the reaction was maintained constant with an accuracy of ±0.5°C using a water thermostat. The process temperature, 50°C, was chosen so as to ensure sufficiently high epoxidation rate, on the one hand, and to reduce the probability of side processes of epoxy ring opening, on the other hand.

The reactor was charged with fatty acid methyl esters of rapeseed, sunflower, and flaxseed oils (0.433, 0.520, and 0.654 mol of double bonds per 100 g of esters, respectively), after which formic acid (10 g, 0.185 mol) was loaded with stirring, and the mixture was stirred until the preset temperature was attained. Then, a 37% aqueous hydrogen peroxide solution (0.23 mol in 20 g of solution) was added through a dropping funnel. The total amount of the aqueous phase loaded was 28 mL. At definite intervals, the reaction was stopped, and the mixture was discharged into a separating funnel, in which it was left for 15–20 min for phase separation and cooling. The phase separation was performed until the phase boundary became clear. After that, the phases were separated, and the reactant concentrations in both phases were determined.

To study the effect exerted by the reactive extraction of aqueous phase components into the organic phase (sunflower oil FAME), we prepared in separate experiments FAME samples with different degrees of epoxidation, following the above-described procedure. After the reaction completion, the organic phase was washed several times with distilled water until pH of the wash waters became equal to 5–6. Then, the residual water was distilled off from the organic layer with a rotary evaporator. After that, a new sample was epoxidized using the similar procedure. After the phase separation, the reactant concentrations in both phases were determined.

The concentrations of formic and performic acids were determined by potentiometric titration. The concentration of hydrogen peroxide was determined by the traditional iodometric titration method. The concentrations of double bonds and epoxy groups were determined by gas–liquid chromatography following the procedure described in [17].

Possible changes in the material balance were analyzed as follows. At definite time moments, we measured the volumes of the separated phases and analyzed them for the content of hydrogen peroxide, formic acid, and performic acid. We also determined the content of epoxy groups and double bonds in the organic phase. The densities of the phases were determined by weighing. In all the experiments, the gravimetric analysis of the phases was performed with the relative uncertainty of up to 1.0%, which allowed us to analyze the molar balance of available oxygen and total acidity for different phases in relation to the temperature and kind of the raw material. The possible causes of deviations from the balance are process loss on reactor walls, partial evaporation of the aqueous phase, and partial decomposition of PFA and HP in the aqueous phase [9].

RESULTS AND DISCUSSION

Before studying kinetic relationships of the process and performing its mathematical modeling, it was necessary to ensure complete coverage of all the processes involved in the phase-transfer epoxidation, including both the main and side reactions. To this end, we first checked the material balances (number of equivalents of protons, oxygen, and double bonds) with respect to the total amount of protons (from the acid and peracid), oxygen $[O]^{\Sigma}$ (incorporated in H_2O_2, HCOOOH, and epoxy group), and double bonds ($[>=<]_0^{\Sigma}$, sum of the running amount and amount consumed for epoxy group formation).

These balances were calculated using the formulas

$$[H^+]^{\Sigma} = ([HCOOH]_w + [HCOOOH]_w)V_w + ([HCOOH]_{org} + [HCOOOH]_{org})V_{org}, \tag{1}$$

$$[O]^{\Sigma} = ([H_2O_2]_w + [HCOOOH]_w)V_w + ([H_2O_2]_{org} + [HCOOOH]_{org} + [epoxy])V_{org}, \tag{2}$$

$$[>=<]_0^{\Sigma} = [>=<]_i + [epoxy]V_{org}, \tag{3}$$

where $[H^+]^{\Sigma}$ is the total number of equivalents of protons (mmol); $[O]^{\Sigma}$, total number of equivalents of H_2O_2, performic acid, and epoxy groups (mmol); ($[>=<]_0^{\Sigma}$), total number of equivalents of double bonds and epoxides (mmol); $[>=<]_i$, running number of equivalents of double bonds (mmol); V_w and V_{org}, volumes of the aqueous and organic phases, respectively (mL); [epoxy], concentration of epoxy groups in the organic phase (M); $[H_2O_2]_w$ and $[H_2O_2]_{org}$, concentrations of hydrogen peroxide (M) in the aqueous and organic phases, respectively; $[HCOOOH]_w$ and $[HCOOOH]_{org}$, concentrations of performic acid (M) in the aqueous and organic phases, respectively; $[HCOOH]_w$ and $[HCOOH]_{org}$, concentrations of formic acid (M) in the aqueous and organic phases, respectively.

When the reaction was performed up to approximately 85% HP conversion, the total proton concentration in both phases, $[H^+]^{\Sigma}$, in all the reactions was preserved. The total number of equivalents of double bonds and epoxides, $[>=<]_0^{\Sigma}$, was preserved also (see table). This fact means that the reaction selectivity with respect to double bonds. $S^{epoxy}_{>=<}$, is very high:

$$S^{epoxy}_{>=<} = \frac{[epoxy]V_{org}}{\left([>=<]_0^{\Sigma} - [>=<]_i^{\Sigma}\right)}. \tag{4}$$

The selectivity of formation of epoxy compounds via double bonds of flaxseed, sunflower, and rapeseed oil was 98–99%. However, the oxygen concentration, $[O]^{\Sigma}$, decreased in the course of the reaction by 25–30% depending on the origin of the ester (see table).

A decrease in the total oxygen concentration, $[O]^{\Sigma}$, in the course of the reaction is due to consumption of available oxygen in other reactions occurring concurrently with the epoxidation. Correlation between the numbers of equivalents of the epoxy groups formed and hydrogen peroxide consumed is more informative. The ratio of these quantities corresponds to the selectivity of epoxy group formation with respect to hydrogen peroxide, $S^{epoxy}_{H_2O_2}$:

$$S^{epoxy}_{H_2O_2} = \frac{[epoxy]V_{org}}{\left([H_2O_2]_0 - [H_2O_2]_i\right)}. \tag{5}$$

For each FAME, the selectivity remains constant throughout the reaction. The selectivity $S^{epoxy}_{H_2O_2}$ somewhat decreases in the series of FAMEs obtained from lineseed (0.78 ± 0.02), sunflower (0.69 ± 0.04), and rapeseed (0.65 ± 0.02) oils (see table). High reliability of the linear correlations ($R^2 = 0.96$–0.99) confirms that the decomposition of peroxy compounds occurs concurrently with the epoxidation.

The revealed influence of the FAME structure on the ratio of the epoxidation and oxygen consumption rates is associated with different influence of the FAME structure on the rates of epoxidation and peroxy compound decomposition. The epoxidation rate increases with increasing amount of double bonds [18], whereas the decomposition rate of peroxy compounds remains constant.

Material balance of epoxidation of FAMEs of vegetable oil at 50°C

Time, min	[>=<], mmol	[epoxy]V_{org}, mmol	([>=<] + [epoxy]V_{org}), mmol	Total acidity $[H^+]^{\Sigma}$, mmol	$[H_2O_2]_i$,[a] mmol	Total oxygen $[O]^{\Sigma}$, mmol
FAME of rapeseed oil						
0	433.0	0	433.0	184.8	217.6	217.6
40	388.8	65.1	422.7	176.6	113.2	191.8
60	379.7	87.5	424.9	175.4	109.3	208.8
80	369.3	101.9	422.7	166.4	62.1	169.9
120	360.2	118.6	422.5	174.3	54.5	179.3
150	347.2	124.9	413.3	169.0	37.1	162.0
FAME of sunflower oil						
0	512.2	0	512.2	184.9	217.6	217.6
20	479.8	32.4	512.2	184.6	147.7	193.3
35	449.9	59.5	509.3	186.6	143.2	193.3
60	433	73.5	506.5	175.6	96.2	176.1
80	412.5	90.5	503.0	184.7	79.4	175.3
130	382.6	120.2	502.8	167.1	41.0	165.2
FAME of flaxseed oil						
0	648.5	0	648.5	186.2	217.6	217.6
20	596.8	38.1	634.9	181.6	187.6	220.0
40	566.9	67.1	634.0	181.4	116.3	191.7
60	556.2	77.2	633.3	178.5	116.2	199.8
100	505.5	123.6	629.1	182.1	66.5	195.5
150	489.9	138.9	628.8	173.8	43.5	184.0

Thus, the result obtained demonstrates the occurrence of hydrogen peroxide or peracid decomposition along commonly known pathways.

High selectivity of formation of epoxy compounds from double bonds of FAMEs prepared from different oils, preserved in time, does not allow estimation of the contribution of another possible reaction, epoxy ring opening with water (or formic acid). In this case, one should expect deviation from the linear correlation because of the superposition of two processes: formation of epoxides and consumption of double bonds in FAME.

Volume and mass balance for aqueous and organic phases. It is known from the literature that the two-phase epoxidation is accompanied by a change in the volume ratio of the aqueous and organic phases. Our experience shows that, when the initial volume of the aqueous phase was small, only a single homogeneous phase was formed by the end of the reaction. Under the conditions of our experiments, the absolute volumes of the phases changed insignificantly, but relative changes were appreciable: The volumes of the aqueous and organic phases changed by more than 20 and by 5–6%, respectively. Because the amounts of aqueous phase components (FA, H_2O_2, and H_2O) are comparable, it can be assumed that considerable loss of the more lyophilic component from the aqueous phase can lead to a significant change in the reactant molar ratios. This fact should affect the kinetics of the peracid formation and, correspondingly, of the process as a whole. Apparently, changes in the phase ratios are due to formation of reaction products, primarily of epoxy groups, making the organic phase less hydrophobic. Therefore, it is also necessary to reveal relationships in variation of the phase volume ratio.

Because all the experimental data were obtained at unchanged epoxidation parameters, we often used the absolute values of the masses (or numbers of equivalents) of the reactants and of the phase volumes for convenience of interpretation of the experimental results in this step of their consideration.

As seen from Fig. 1, the organic phase volume V_{org} increases with the progress of the reaction and formation of epoxy compounds. The aqueous phase volume V_{w} simultaneously decreases.

The correlations between the absolute values of V_{org} or V_{w} and the number of equivalents of epoxy groups formed in the organic phase, [epoxy]V_{org}, are linear with $R^2 = 0.7$ and 0.8, respectively:

$$V_{\mathrm{org}} = 113.0 + (0.038 \pm 0.003)[\mathrm{epoxy}]V_{\mathrm{org}}\ (\mathrm{mL}), \tag{6}$$

$$V_{\mathrm{w}} = 25.0 - (0.031 \pm 0.003)[\mathrm{epoxy}]V_{\mathrm{org}}\ (\mathrm{mL}). \tag{7}$$

The absolute term in these equations should correspond to the initial phase volume. This is true for the organic phase, but for the aqueous phase the initial volume decreased by approximately 10%, from 28 to 25 mL. This difference may be due to partial solubility of formic acid in FAME already at the moment of mixing the solutions. As will be shown below, the amount of formic acid that passed into the aqueous phase depends on the FAME structure insignificantly. The initial change in the organic phase volume is insignificant against the background of the measurement uncertainty.

The slopes of the V_{org}–[epoxy] and V_{w}–[epoxy] correlations correspond to changes in the volume of each phase per unit of the epoxy compound formed (ΔV_{w} and ΔV_{org} for the aqueous and organic phases, respectively). It should be noted that their numerical values appreciably differ from each other. As can be seen, the loss in the aqueous phase volume is smaller in the absolute value than the gain in the organic phase volume. This effect is not an artifact, because there is satisfactory ($R^2 = 0.7$) linear correlation between changes in the volumes of both phases:

$$\Delta V_{\mathrm{org}} = (0.87 \pm 0.08)\Delta V_{\mathrm{w}}\ (\mathrm{mL}). \tag{8}$$

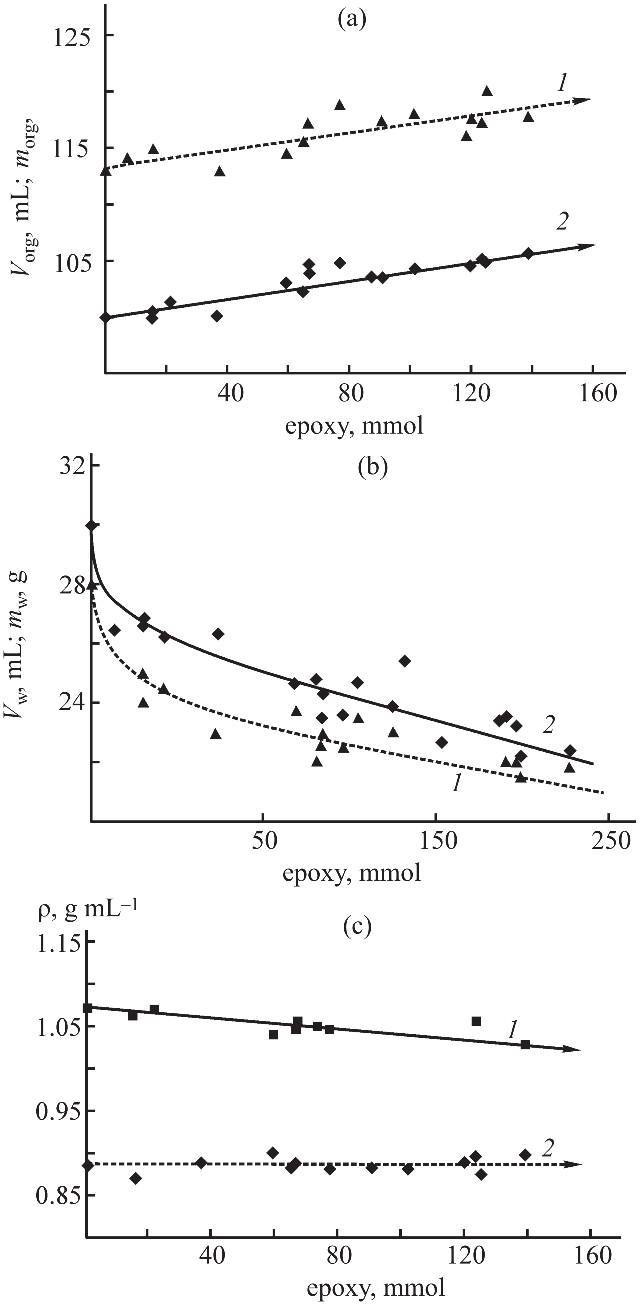

Fig. 1. Variation of the (*1*) volumes V_{w}, V_{org} and (*2*) weights m_{w}, m_{org} of the (a) organic and (b) aqueous phases in the course of epoxidation in relation to the number of equivalents of epoxy groups formed (epoxy) and (c) concomitant variation of the density ρ of (*1*) aqueous and (*2*) organic phases.

Expansion of the volume of the components coming to the organic phase from the aqueous phase is associated with different densities of the aqueous and organic phases. The density of the organic phase does not noticeably change in the course of the reaction (Fig. 1). However, the density of the aqueous phase

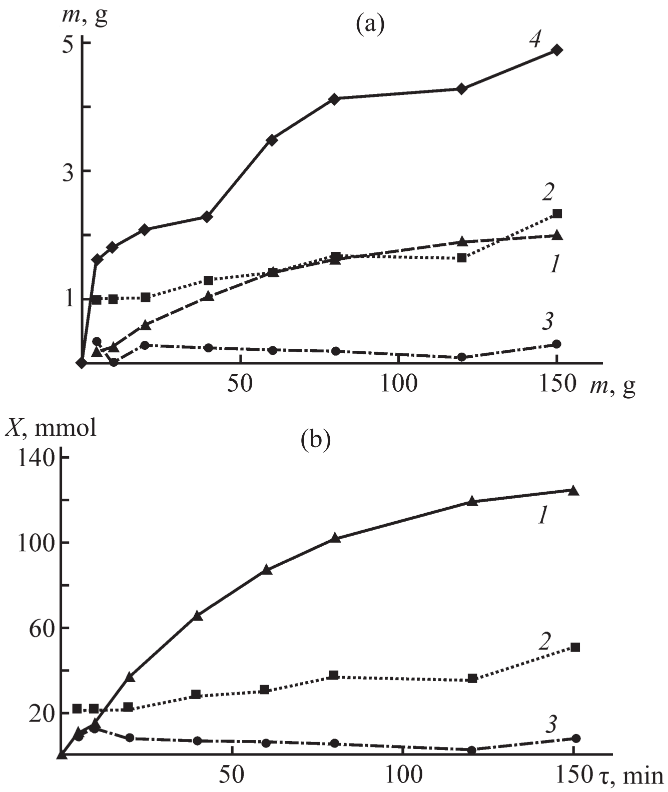

Fig. 2. Changes in the reactant amounts (a) *m* and (b) *X* in the organic phase in the course of epoxidation. (τ) Time. (*1*) Epoxide oxygen, (*2*) FA, (*3*) H_2O_2, and (*4*) total weight gain.

slightly decreases (from $d_4^{20} = 1.08$ to $d_4^{20} = 1.03$) owing to conversion of heavier hydrogen peroxide ($d_4^{20} = 1.45$) into water ($d_4^{20} = 0.998$). This fact, however, will not alter the relationship $\Delta V_w > \Delta V_{org}$.

The changes in the phase volumes are undoubtedly influenced by the fact that peroxide oxygen incorporated in hydrogen peroxide (aqueous phase) passes into the organic phase upon formation of epoxy groups. Actually this is the phase transfer of a significant amount of bound oxygen, causing changes in the volumes and densities of the phases. Under the conditions of our experiments, the amount of the initial oxygen in hydrogen peroxide was 3.47 g (~0.22 mol). Taking into account the loss of the total oxygen $[O^+]^\Sigma$ (see table), the organic phase weight after the reaction completion should increase by approximately 2.4 g at the expense of oxygen in epoxy groups, or by 2.7 mL taking into account the organic phase density. However, the experimentally determined total weight gain of the organic phase was approximately 2 times larger, 5 g (Fig. 2), which rules out the simplified interpretation of changes in the phase volume ratio upon epoxidation with the peracid formed in situ.

To determine the causes of this phenomenon more accurately, it was necessary to consider in detail the relationships of the redistribution of each reactant between the phases. Analysis of the aqueous phase before and after the reaction revealed the presence of FAMEs and their epoxidized derivatives in trace amounts. Apparently, the above-noted transfer of aqueous phase components into the organic phase is not restricted to the transfer of peroxide oxygen from the aqueous phase to the organic phase upon formation of epoxy groups. The concomitant change in the organic phase hydrophobicity also plays an important role.

CHANGE IN THE ORGANIC PHASE HYDROPHOBICITY

FA extraction. The above data demonstrate a complex pattern of the phase volume redistribution in the two-phase epoxidation reaction due to formation of epoxy compounds and their accumulation in the organic phase. Along with changes in the volumes of both phases, caused by the transfer of peroxide oxygen from the aqueous phase to the organic phase (in the form of oxygen atoms incorporated in epoxy groups), formic acid is also involved in the phase transfer, altering the phase volumes to a comparable extent.

As noted above, the phase redistribution of formic acid partially occurs already on mixing the solutions (Fig. 2, curve *2*) owing to the presence of an ester group in FAMEs [19]. It is known that fatty acid esters such as, e.g., ethyl hexanoate efficiently extract formic acid from aqueous solutions [20].

In addition, the amount of the initially extracted FA depends on the content of double bonds in FAME and increases in going from rapeseed to sunflower and then to flaxseed oil derivatives (Fig. 3). The differences in the distribution ratios of formic acid, D^{FA}, for different esters are probably caused by the dependence of the FAME molecule polarity on the number of double bonds and by specific interactions of formic acid with π systems. The nature of interaction of formic acid with π systems of such compounds as acetylene or benzene is being actively studied now [21, 22]. This assumption is indirectly confirmed by the fact that the order at which FAMEs are ranked with respect to the extracting ability coincides with the order in which the FAME retention time in gas–liquid chromatography increases, because in these cases the interactions of FAME with FA and with the polar liquid phase of the chromatographic column are similar in nature [23].

With the progress of formation of epoxy compounds, the formic acid distribution ratio D^{FA} linearly increases, but this trend is independent of the kind of FAME. For the system of formic acid (85% aqueous solution) and FAMEs with different degrees of epoxidation, the correlation has the form

$$D^{MK} = \frac{[HCOOH]_{org}}{[HCOOH]_w} = \left(\begin{bmatrix} 0.035 \\ 0.04 \\ 0.047 \end{bmatrix} + 0.041[\text{epoxy}] \right). \quad (9)$$

The absolute terms of Eq. (9) correspond to the equilibrium distribution ratios of formic acid, D^{FA}, in individual FAMEs from rapeseed (0.035), sunflower (0.04), and flaxseed (0.047) oils.

H_2O_2 extraction. The phase transfer of hydrogen peroxide occurs to a lesser extent. At the beginning of the process, its concentration in the organic phase increased, passed through a maximum, and decreased by the end of the reaction virtually to zero.

Such a trend in variation of the H_2O_2 concentration corresponded to H_2O_2 redistribution between the phases in the course of equilibrium formation of the peracid, followed by the H_2O_2 consumption for the epoxidation. Using the analytical data for the aqueous phase, we calculated the H_2O_2 distribution ratios in the course of the reaction. As we found, the numerical values of $D^{H_2O_2}$ increased with the progress of the reaction and with an increase in the content of epoxy groups, i.e., the trend was the same as in extraction of formic acid. Additional experiments on the distribution of reaction components in the individual system of water with sunflower oil FAMEs have shown that the hydrogen peroxide distribution ratio $D^{H_2O_2}$ linearly correlates with the concentration of epoxy groups in the organic phase (Fig. 4). The pattern is essentially the same as that observed in the course of epoxidation:

$$D^{H_2O_2} = \frac{[H_2O_2]_{org}}{[H_2O_2]_w} = (0.011 + 0.0045[\text{epoxy}]). \quad (10)$$

H_2O extraction. The third component of the aqueous reaction system is water. Water does not noticeably dissolve in FAMEs: The distribution ratio D^{H_2O} is as low as 5×10^{-5}. However, it sharply increases as compounds with epoxy groups appear in the organic phase (Fig. 5).

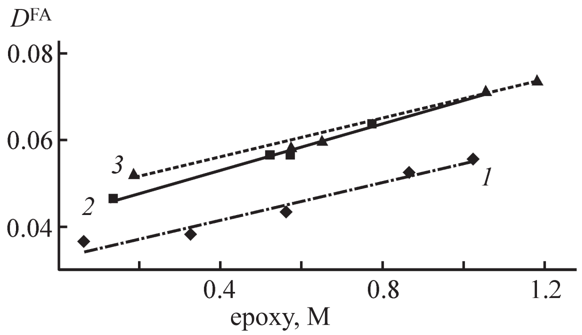

Fig. 3. Formic acid distribution ratio D^{FA} as a function of the concentration of epoxy groups (epoxy) in FAME prepared from (*1*) rapeseed, (*2*) sunflower, and (*3*) flaxseed oils.

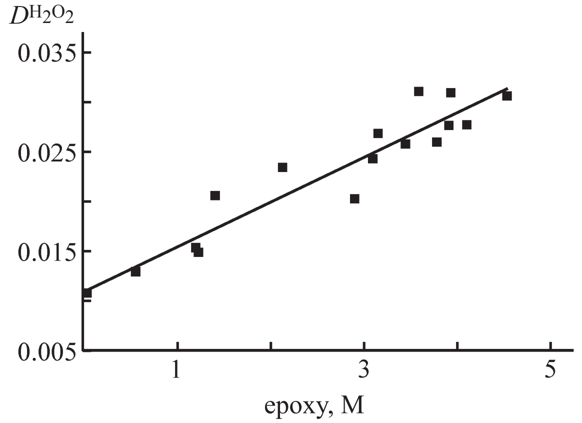

Fig. 4. Variation of the distribution ratio $D^{H_2O_2}$ in the course of epoxidation of sunflower oil FAME in relation to the concentration of epoxy groups (epoxy) in the organic phase.

Formation of stable low-polarity 1 : 1 and 1 : 2 adducts of epoxy groups with water has been well studied for propylene oxide as example [24]. Therefore, it is not surprising that the water distribution ratio in the system consisting of aqueous formic acid solution (~30 wt %) and sunflower oil FAME samples with different degrees of epoxidation is described by a quadratic function

$$D^{H_2O} = \frac{[H_2O]_{org}}{[H_2O]_w} = (5 + 100[epoxy] + 50[epoxy]^2) \times 10^{-5}. \quad (11)$$

The quadratic dependence of the water distribution ratio can formally suggest the formation of, e.g., adducts of two epoxy groups with one molecule of extracted water, which is certainly improbable. On the other hand,

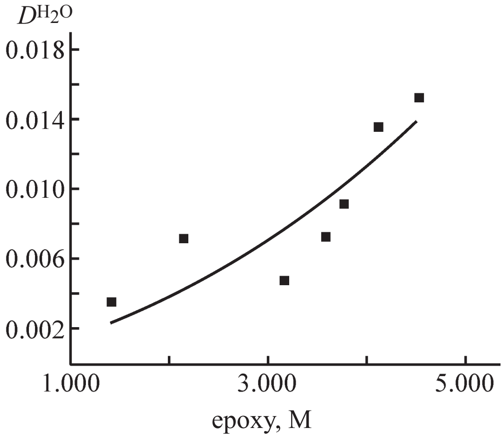

Fig. 5. Correlation between the water distribution ratio D^{H_2O} and concentration of epoxy groups (epoxy) in the organic phase (with sunflower oil FAME as example).

the effect of formic acid whose concentration in the organic phase also increases owing to an increase in the content of epoxy groups should be taken into account. Formic acid in the organic phase can also act as extractant in reactive extraction of water into epoxidized FAMEs. In this case, there should be quadratic dependence of the water distribution ratio owing to the formation of ternary adducts of type formic acid–water–epoxy group.

The equilibrium phase distribution of formic acid under steady-state conditions was not considered because of its high reactivity and methods used for studying the phases (the phase separation takes certain time).

Discussion of the organic phase hydrophobicity. Mechanism of reactive extraction. Analysis of the physicochemical features of the two-phase epoxidation with performic acid formed in situ revealed two main causes of changes in the phase volumes, leading to comparable results of transfer of the aqueous phase components. Along with the transfer of peroxide oxygen from H_2O_2 present in the aqueous phase into the organic phase, associated with the formation of epoxy groups in the organic phase, lyophobic components of the aqueous phase (formic acid, water, and hydrogen peroxide) undergo reactive extraction. Therefore, it is not surprising that the aqueous phase can completely disappear by the end of epoxidation if the initial ratio of the organic and aqueous phases is sufficiently high. Apparently, the formed epoxy groups of FAME act as extractant. The correlation of the distribution ratios of formic acid [Eq. (9)], hydrogen peroxide [Eq. (10)], and water [Eq. (11)] with the amount of epoxy groups in the organic phase is associated with the formation of adducts of the extractant with the aqueous phase components: {FA : epoxy }, {H_2O_2 : epoxy}, {H_2O : epoxy}, and {FA : H_2O : epoxy}.

As shown by experimental methods [25], different adducts of formic acid monomers and dimers with several water molecules only slightly differ from each other in energy [26]. Usually the transfer of carboxylic acids from an aqueous phase into a hydrophobic medium is associated with the formation of low-polarity cyclic dimers [27] or stable spherical microsolvates of formic acid dimer with five water molecules [28].

Dimers are relatively well solvated in a nonpolar medium [29], which leads to an increase in the formic acid distribution ratio in going to more concentrated solutions. However, in our case the idea of the role of the acid dimers in the extraction is true only in part. The FA distribution ratio sharply increases only at the FA concentration in the aqueous phase increased to more than 5 M.

Published data on the FA distribution ratios usually cover formic acid solutions of intermediate concentrations (3–10 M). It is noted that the distribution ratios are virtually independent of the acid concentration. For example, the D^{FA} values for the extraction with soybean oil FAME [30] are in good agreement with the results of this work. The data from [30] are compared with our data in Fig. 6. As can be seen, the data fairly well coincide with each other, differing only in the range of dilute solutions ([HCOOH] < 2.0 M). At low FA concentrations, the distribution ratio starts to increase with the dilution of the acid solution, and the FA concentration interval ~3–10 M corresponds to a broad minimum of the dependence. The more dilute is the aqueous FA solution, the more efficient is the FA extraction with FAME esters. The dilution effect is not due to changes of the solution acidity in the interval $1.2 < pH < 4.0$ [31]. Apparently, complex concentration dependence of D^{FA} is associated with the structure of different formic acid solvates.

Increased distribution ratio of formic acid in strongly diluted solutions is noted in many papers [20]. As the solution concentration is increased, D^{FA} decreases, reaching a minimum in the above-noted range [32]. The explanation to this fact is quite simple. As the water amount in formic acid solutions is increased, the total number of low-polarity solvates (clusters) of formic acid with water of the composition from 1 : 1 to 1 : 5

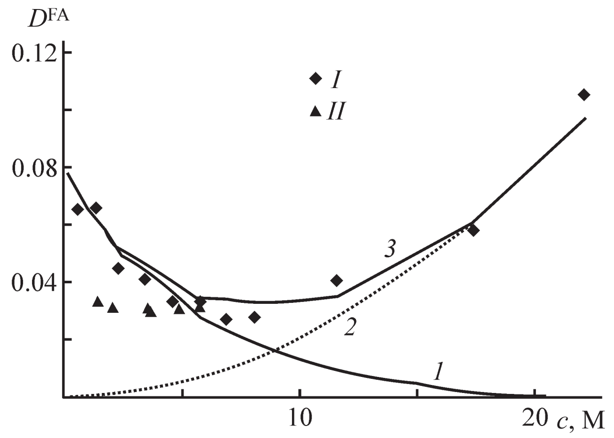

Fig. 6. Comparison of the experimental distribution ratios D^{FA} in sunflower oil FAME as functions of the initial FA concentration *c* in the aqueous phase. (*I*) Data of this work, (*II*) data of [30], (*1*, *2*) normalized asymptotes of the dependences $D^{FA} = 9 \times 10^{-9}[H_2O]^4$ and $D^{FA} = 2 \times 10^{-4}[HCOOH]^2$, and (*3*) calculated data (superposition of curves *1* and *2*).

increases, or, e.g., stable spherical microsolvates of formic acid dimer with four or five water molecules are formed [28]. An increase in the concentration of the clusters can favor their transfer into a low-polarity medium such as, e.g., epoxidized FAMEs. Both free hydroxy groups of the solvates and “acidic” H–C bond of formic acid are probably involved in the interaction of aqueous formic acid clusters with the epoxy group [33].

The formal mathematical description of the dependence shown in Fig. 6 qualitatively confirms the suggested mechanism of changes in D^{FA}. The left branch of the experimental points is described by the function $D^{FA} = \alpha[H_2O]^4$, and the right branch, by the function $D^{FA} = \beta[HCOOH]^2$, where α and β are equal to 9×10^{-9} L^4 mol^{-4} and 2×10^{-4} L^2 mol^{-2}, respectively, i.e., the formal polynomial dependences describe the variation of the concentrations of the corresponding water and formic acid clusters and are proportional to the corresponding distribution constants of these clusters.

As noted above, the phase distribution of performic acid was not considered, but there are good grounds to assume that the distribution ratio of formic acid also increases with the progress of the epoxy compound formation. This idea is reflected in a patent concerning a procedure for vegetable oil epoxidation [15], in which it is suggested that the reaction product, the corresponding epoxide, be initially added to the reaction mixture to increase the extraction of performic acid formed in situ in the aqueous phase.

CONCLUSIONS

The above-considered relationships of the redistribution of the reaction mixture components between the phases in epoxidation of fatty acid methyl esters of vegetable oil with performic acid in situ confirm the occurrence of the reactive extraction of the reactants and reaction products with the epoxy compounds formed. This fact should be taken into account in mathematical description of peracid epoxidation processes.

ACKNOWLEDGMENTS

The authors are grateful to the Russian Foundation for Basic Research and to the Ministry of Education and Science of the Russian Federation for the financial support (assignment no. 4.2512.2014/K).

REFERENCES

1. Medina Gonzalez, Y., De Caro, P., Thiebaud-Roux, S., and Lacaze-Dufaure, C., *J. Solution Chem.,* 2007, vol. 36, pp. 437–446.
2. Galli, F., Nucci, S., Pirola, C., and Bianchi, C.L., *Chem. Eng. Trans*., 2014, vol. 37, pp. 601–606.
3. Voronov, M.S., Sapunov, V.N., Makarov, A.A., et al., *Russ. J. Appl. Chem*., 2016, vol. 89, no. 3, pp. 421–431.
4. Derawi, D., Salimon, J., and Ahmed, W.A., *Malaysian J. Anal. Sci*., 2014, vol. 18, no. 3, pp. 584–591.
5. Turco, R., Vitiello, R., Russo, V., et al., *Green Process Synth.,* 2013, vol. 2, pp. 427–434.
6. Santacesaria, E., Tesser, R., Di Serio, M., et al., *Chem. Eng. J.,* 2011, vol. 173, pp. 198–209.
7. Lehnen, D.R., Guzatto, R., Defferrari, D., et al., *Environ. Chem. Lett.,* 2014, vol. 12, no. 2, pp. 335–340.
8. Hong, L.K., Yusop, R.M., Salih, N., and Salimon, J., *Malaysian J. Anal. Sci.,* 2015, vol. 19, no. 1, pp. 144–154.
9. Leveneur, S., Zheng, J., Taouk, B., et al., *J. Taiwan Inst. Chem. Eng*., 2014, vol. 45, no. 4, pp. 1449–1458.
10. Hong, Y.K., Hong, W.H., and Han, D.H., *Biotechnol. Bioprocess Eng.,* 2001, vol. 6, no. 6, pp. 386–394.
11. Uslu, H., *Sep. Sci. Technol*., 2009, vol. 44, pp. 1784–1798.
12. Datta, D., Kumar, S., and Uslu, H., *J. Chem*., 2015, pp. 1–16.
13. He, W., Fang, Z., Ji, D., et al., *Org. Process Res. Dev.,* 2013, vol. 17, no. 9, pp. 1137–1141.
14. De Quadros, J.V., Jr. and Giudici, R., *Chem. Eng. Process*., 2016, vol. 100, pp. 87–93.

15. RF Patent 2058308, Publ. 1996.
16. Hang, X. and Yang, H., *J. Am. Oil Chem. Soc.,* 1999, vol. 76, pp. 89–92.
17. Voronov, M.S., Gustyakova, S.I., Kulazhskaya, A.D., et al., *Usp. Khim. Khim. Tekhnol.,* 2016, vol. 30, no. 11, pp. 17–18.
18. La Scala, J. and Wool, R.P., *J. Am. Oil Chem. Soc.,* 2002, vol. 79, no. 4, pp. 373–378.
19. Timedjeghdine, K.M., Hasseine, A., Binous, H., et al., *Fluid Phase Equil.,* 2016, vol. 415, pp. 51–57.
20. Demirel, G. and Gehreli, S., *Fluid Phase Equil.,* 2013, vol. 356, pp. 71–77.
21. George, L., Sanchez-García, E., and Sander, W., *J. Phys. Chem. A,* 2003, vol. 107, pp. 6850−6858.
22. Banerjee, P., Bhattacharya, I., and Chakraborty, T., *J. Phys. Chem. A,* 2016, vol. 120, no. 20, pp. 3731–3739.
23. Carvalho, M.S., Mendonça, M.A., Pinho, D.M.M., and Resck, I.S., *J. Braz. Chem. Soc.,* 2012, vol. 23, no. 4, pp. 763–769.
24. Zheng, S., Borho, N., and Xu, Y., *J. Am. Chem. Soc.,* 2006, vol. 128, no. 51, pp. 17126–17131.
25. Marushkevich, K., Siltanen, M., Rasaanen, M., et al., *J. Phys. Chem. Lett.,* 2011, vol. 2, pp. 695–699.
26. Chen, J., Brooks, C.L., and Scheraga, H.A., *J. Phys. Chem. B,* 2008, vol. 112, pp. 242–249.
27. Marushkevich, K., Khriachtchev, L., Rasänen, M., et al., *J. Phys. Chem. A,* 2012, vol. 116, pp. 2101−2108.
28. Nordstrom, C.M., McGrath, A.J., and Thakkar, A.J., *Can. J. Chem.,* 2010, vol. 88, pp. 736–743.
29. Wasewar, K.L., *J. Chem. Eng. Appl.,* 2012, vol. 3, no. 4, pp. 249–255.
30. Campanella, A., Fontanini, C., and Baltanas, M., *Chem. Eng. J.,* 2008, vol. 144, pp. 466–475.
31. Seyd, A.H., Lanez, T., and Belfar, M.L., *Asian J. Chem.,* 2012, vol. 24, no. 10, pp. 4511–4516.
32. Cai, W., Zhu, S., and Piao, X., *J. Chem. Eng. Data,* 2001, vol. 46, pp. 1472–1475.
33. Borho, N. and Xu, Y., *Angew. Chem.,* 2007, vol. 119, no. 13, pp. 2326–2329.